PB85-113033

Method 16A for Determination of Total Reduced Sulfur Emissions Summary of Comments and Responses

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Oct 84

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/3-82-028	2.	3. RECIPIENT'S ACCESSION NO. PB85 113033
4. TITLE AND SUBTITLE Method 16A for ~~the~~ Determination of Total Reduced Sulfur Emissions Summary of Comments and Responses		5. REPORT DATE October 1984 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Emission Standards and Engineering Division		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Emission Measurement Branch (MD-19) Emission Standards and Engineering Division U. S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS DAA for Air Quality Planning and Standards (MD-10) Office of Air and Radiation U. S. Environmental Protection Agency Research Triangle Park, N. C. 27711		13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document addresses the public comments submitted after proposal of Method 16A in the Federal Register. Changes made to the method as a result of these comments are included. This document serves as the basis for the revisions which have been made to the test method between proposal and promulgation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
		13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release Unlimited	Unclassified	19
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

PB85-113033

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

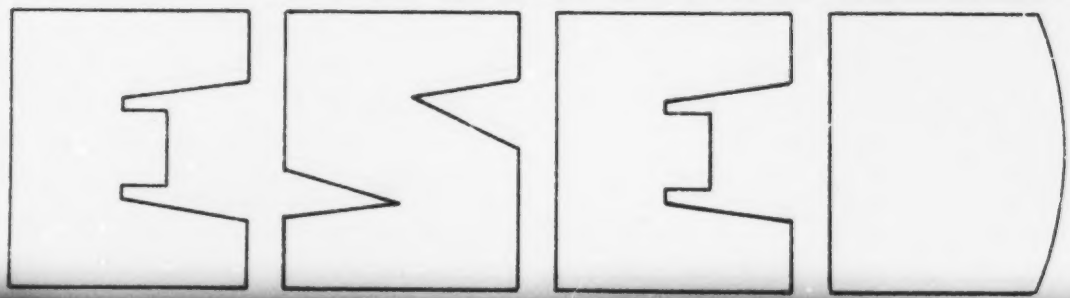
EPA-450/3-82-028
October 1984

Air

EPA

Method 16A for Determination of Total Reduced Sulfur Emissions - Summary of Comments and Responses

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161



EPA-450/3-82-028

Method 16A for Determination of Total Reduced Sulfur Emissions - Summary of Comments and Responses

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

October 1984

This report has been reviewed by the Emission Standards and Engineering Division of the Office of Air Quality Planning and Standards, EPA, and approved for publication. Mention of trade names or commercial products is not intended to constitute endorsement or recommendation for use. Copies of this report are available through the Library Services Office (MD-35), U.S. Environmental Protection Agency, Research Triangle Park, N.C. 27711, or from National Technical Information Services, 5285 Port Royal Road, Springfield, Virginia 22161.

TABLE OF CONTENTS

		Page
Chapter 1.	INTRODUCTION	1
Chapter 2.	SUMMARY OF CHANGES SINCE PROPOSAL.	2
Chapter 3.	SUMMARY OF PUBLIC COMMENTS AND RESPONSES	4
	Table 1. LIST OF COMMENTERS	18

Chapter 1

INTRODUCTION

On June 18, 1981, the U.S. Environmental Protection Agency published Method 16A, "Determination of Total Reduced Sulfur Emissions from Stationary Sources," in the Federal Register (46 FR 31904). This method can be used by affected facilities to determine compliance with the regulations. This method was proposed under the authority of Sections 111, 114, and 301(a) of the Clean Air Act, as amended.

Public comments were solicited at the time of proposal. An invitation to request a public hearing was issued to provide interested persons the opportunity for oral presentation of data, views, or arguments concerning the proposed test method, but no person desired to make an oral presentation. The public comment period was from June 18, 1981, to August 17, 1981.

Letters concerning issues relative to the proposed test method were received from 10 commenters. A detailed discussion of these comments and responses are summarized in this document. The summary of comments and responses serve as the basis for the revisions which have been made to the test method between proposal and promulgation.

Chapter 2

SUMMARY OF CHANGES SINCE PROPOSAL

1. Section 1. A new section discussing interferences, precision and bias has been added.

2. Section 1.1. New minimum detection limits for the method when sampling for 1 and 3 hours have been added.

3. Section 2. The probe specifications have been changed to minimize the sampling of particulates. A heated filter has been added to the sampling train.

4. Section 2.1. A 250-ml polyethylene bottle is needed for the peroxide solution recovery.

5. Section 2.1.1. The two midget impingers used for the SO_2 scrubber have been replaced by three larger Teflon impingers.

6. Section 2.1.3. The combustion tube furnace should be capable of maintaining a temperature of 800 $\pm$ 100 °C instead of 815 $\pm$ 15 °C.

7. Section 2.1.4. The rate meters should be capable of measuring flow rate to within 5 percent of the selected flow rate.

8. Section 2.3. The 10-ml buret should have 0.05 ml graduations.

9. Section 3.1.3. A pH adjustment of the citrate buffer solution is required.

10. Section 3.1.4. The standard deviation for Method 11 analyses of the calibration gas is specified. Gravimetrically calibrated permeation devices are an allowable option for generating the calibration gas. The gas concentration should be generated in the range of the stack concentration or within 20 percent of the applicable standard level.

11. Section 3.1.5. For the combustion gas, an example system for purifying ambient air is listed.

12. Section 4.1. An SO_2 scrubber conditioning period is specified.

13. Section 4.1.1. New directions for the SO_2 scrubber are given. The oxidation furnace temperature is maintained at 800 $\pm$ 100°C.

14. Section 4.1.3. The sample is collected over a 1- or 3-hour period. The three-hour sample should not be intermittent and should have a total volume of 360 liters. It is recommended that the probe be washed, the filter replaced, and the SO_2 scrubber changed after each test run.

15. Section 4.3. The sample analysis has been modified to allow for duplicate analysis.

16. Section 5.2. The performance check calibration system has been changed by replacing the dry gas meters used to measure the calibration and combustion gases with calibrated rotameters. The results of the recovery check will be reported but will not be used to correct the emission data. A recovery of 100 $\pm$ 20 percent must be obtained for the data to be valid. The performance check prior to testing is recommended but is not mandatory, and no precision for this check is specified.

17. Section 6. This section has been expanded to include sample volume, TRS concentration, and recovery check calculations.

18. Section 7. Two additional references have been added to the bibliography.

Chapter 3

SUMMARY OF PUBLIC COMMENTS AND RESPONSES

Method 16A

1. D-2

Comment: The definition of total reduced sulfur compounds (TRS) in 40 CFR 60.281 does not make reference to Method 16A. This should be done or mention of Method 16 should be dropped.

Response: Mention of Method 16 is essential in defining the individual components that make up TRS because the compounds are identified using gas chromatography. Since Method 16A is an alternative method and makes no distinction between sulfur compounds, there is no advantage in including it in the definition.

2. D-2

Comment: When calculating compliance with § 60.283(a)(4), a total mass emission rate is needed and relies on the known concentration of each reduced sulfur compound. Since Method 16A oxidizes all sulfur compounds to sulfur dioxide before analysis, the concentrations needed in § 60.285(d)(3) are not available.

Response: Section 60.285(d)(3) is being revised to allow the calculation of TRS concentrations on an equivalent H_2S basis. This revision was proposed in the Federal Register on January 19, 1984 (49 FR 2448) and will eliminate the need to quantify individual TRS compounds.

3. D-5, D-6, D-8, D-9

Comment: The following changes or additions are recommended for the SO_2 scrubber system.

a. The specified 40 ml of citrate scrubber solution may not be sufficient to collect high levels of SO_2 for extended periods of time. Two large impingers containing 200 ml of scrubber each will effectively remove the SO_2.

b. The midget impingers will not have the capacity to hold the volumes of condensed moisture present in the streams of some sources.

c. The pH of the scrubber solution should be adjusted to 5.5 - 5.6 with citric acid or potassium citrate.

d. The scrubber should be conditioned with 5 to 10 ppm H_2S in nitrogen or source gas for 15 minutes prior to initiation of sampling.

Response: The scrubber system has been changed to use three large Teflon impingers in series. The first two impingers will contain 100 ml of scrubber solution each, while the third impinger will be initially dry. An addition to Section 3.1.2 has been made requiring the pH adjustment of the scrubber solution. A requirement to condition the scrubber before sampling has also been added. Our studies show that a 10-minute purge with stack gas provides sufficient conditioning.

4. D-5, D-8

Comment: In the background paper referenced in Section 7.1, it is indicated that 83 ppm H_2S is completely oxidized at 2 liters per minute but not at 3 liters per minute with the furnace temperature at 850°C. An earlier study suggests a temperature of 1000°C for the oxidation of TRS compounds. The testing reported in the background paper also primarily used H_2S. It would appear that additional effort should be spent in optimizing the oxidation temperature and flow rates for complete conversion of mixtures of TRS compounds.

Response: Studies by the EPA and other sources have shown that temperatures significantly lower than 850°C will completely oxidize TRS compounds at levels encountered at most sources. A temperature range of 800 ± 100 °C will be specified for the oxidation furnace. The data listed in the background paper included one sample set that showed complete oxidation of a mixture of TRS compounds. Other laboratory studies have verified the complete oxidation of all TRS compounds at the 2 liter per minute flow rate.

5. D-8

Comment: Specifying a combustion furnace temperature of 815 ± 15°C in Section 2.1.3 is not critical. Our studies indicate that 460°C is sufficient to oxidize all TRS compounds.

Response: We agree that the ±15°C range is not critical, but to maintain uniformity in application, the furnace temperature range will be specified as 800 ± 100 °C.

6. D-5

Comment: At some facilities, the tube furnace may not be permitted due to safety restrictions.

Response: At facilities where this alternative method is restricted, Method 16 should be used.

7. D-5

Comment: In the background paper referenced in Section 7.1, the results of a field study are presented wherein Method 16A is compared to Method 16 and the Barton Coulometric Method at a lime kiln, recovery furnace, and smelt dissolving tank. From the data, it is very clear that Methods 16 and 16A do not give the same results on the kiln emissions. The report states

that the difference was caused by CO_2 quenching of the photometric detector used in Method 16, whereas Method 16A is not affected by CO_2. The emission standard for pulp mills, however, is stated to be 5 ppm of TRS emissions based on the use of reference Method 16. If Method 16A does not give comparable results to the reference method, it cannot be used to regulate emissions at this source without either changing the standard by specifying different values for the method or by revising the reference method. The values obtained on the H_2S calibration standards during the field work indicate that both methods give low values. In comparison, in the laboratory portion of the study, high values were obtained by Method 16A. Further study is needed in this area.

Response: Method 16 lists CO_2 as having a substantial desensitizing effect on the flame photometric detector and states that acceptable systems must demonstrate that they have eliminated this interference. The Method 16 system used at the lime kiln had not corrected this CO_2 problem; hence, the values it gave were substantially lower than those obtained using Method 16A. The values obtained for the field calibration gases show that both methods had recoveries around 90 percent. Recoveries above 80 percent are acceptable. The recoveries for the Method 16A laboratory sample sets averaged 102 percent, with all sets within 9 percent of the known sample value.

Method 16A is proposed as an alternative method. This does not require equivalency to Method 16, but that the method produce results adequate to determine compliance.

8. D-5

Comment: A considerably longer sampling time should be used in order to provide a higher concentration sample that would reduce errors due to the small amount of titrant needed, the faintness of the indicator endpoint, and other errors common to sampling.

Response: Laboratory and field studies have shown that Method 16A can accurately measure TRS in the range of the emission standards when 1- or 3-hour samples are taken. If a 1-hour sample is collected from a source emitting 5 ppm TRS, the amount of titrant needed for analysis would be approximately 2 ml. This titration volume can be accurately measured to within 0.025 ml using the buret specified in the method. The precision in distinguishing the indicator endpoint for an experienced analyst is normally within 1 drop (0.05 ml) of titrant. Therefore, the error associated with this small titrant volume (less than 2 percent) and indicator endpoint detection (2.5 percent) should be less than 5 percent.

9. D-8

Comment: The amount of thorin indicator added for titration is critical to the end point. Consistency should be used for blanks and samples.

Response: Four drops will be specified for samples and blanks.

10. D-5, D-6, D-7, D-8, D-9

Comment: More flexibility should be allowed in the calibration system. The use of permeation devices should be permitted in place of the cylinder gas for the following reasons:

a. Method 16 uses permeation tubes.

b. Gas cylinders are not as safe as permeation systems.

c. It is difficult to accurately analyze H_2S cylinder gas by Method 11 when the concentration is less than 50 ppm. This would affect the ability to meet the $\pm$15 percent accuracy criterion specified in the method.

d. The dilution required to bring 30 to 50 ppm H_2S into the applicable range would introduce significant errors.

e. If desired, H_2S from cylinders can be calibrated against permeation tubes traceable to the National Bureau of Standards (NBS). This would eliminate the need for dilution.

Response: Permeation devices will be allowed as alternative calibration systems as long as they meet the performance check of Section 4.3. A recent EPA study evaluating Method 11 placed the minimum detectable limit at 2.4 ppm and showed that accurate analyses could be performed in the 2-20 ppm range. The Method 11 analysis is required due to the instability of cylinder gas H_2S over periods of time. The $\pm$ 15 percent accuracy criterion has been changed to $\pm$ 20 percent.

11. D-6, D-8, D-9

Comment: The field calibration system includes two gas cylinders and two dry gas meters. It is fairly complex and requires adjusting several flows and then taking simultaneous meter readings when starting and stopping. The dilution factor cannot be accurately determined because it is calculated by taking the difference between two large volumes. This setup should be listed as an example system only. A setup that has been shown to work,

uses a rotameter to monitor the flow from the H_2S cylinder and a dry gas meter to record the total flow. The flow rate through the rotameter will remain constant during sample recovery checks.

Response: The proposed calibration system has been revised to make it simpler and less prone to inaccuracies. The new example system utilizes calibrated rotameters to set the H_2S and combustion gas flow rates. This will eliminate the need for dry gas meters to determine the individual volumes of these gases. Alternative systems may be used provided the acceptability criteria of Section 4.3 is met.

12. D-6, D-9

Comment: The post-test procedure calls for introducing the recovery gas through the probe. This is different from the more desirable Method 16 requirement of introducing the gas after the probe and filter. Why was this change made? If the probe is heated, there should be no TRS loss. This post-test loss check should be performed after each third sample or earlier, if desired.

Response: It has been found that components emitted by some facilities may collect in the probe and attribute to significant TRS losses through adsorption. This loss can be effectively determined by including the uncleaned probe in the post-test procedure. This loss check through the probe is not required for Method 16 because higher sampling rates are employed and a very large amount of calibration gas would be needed.

Field tests have shown that one field recovery sample after each test run is sufficient when using the modified probe design, the heated in-line

filter, and when changing the SO_2 scrubber after each run. Recovery checks performed on a more frequent basis are allowed.

13. D-6, D-8

Comment: Section 4.1.3 requires that a run consists of three 1-hour samples or one 3-hour sample to be consistent with Method 16. One 3-hour sample would not give any indication of precision. Also, Method 16 needs a 3-hour run to get a reasonable average of 16 individual injections. A 2-hour run has been found ideal since three can be performed in addition to calibration in a single day, whereas the 3-hour runs would require an additional day. A continuous sample for 2 hours gives a better average than sixteen 10-second grab samples and does not invalidate the intent of Method 16.

Response: The test run time was chosen primarily to be consistent with reference Method 16 since this is an alternative method. A shorter time would offset the similarity of the two methods.

Neither a 2- nor 3-hour sample would give any indication of precision. The option to collect one continuous 3-hour sample as opposed to three individual 1-hour samples may be preferred in certain situations.

14. D-6

Comment: More flexibility to use different apparatus should be allowed provided the quality assurance tests are met.

Response: This flexibility is allowed and is stated in Section 2.1.

15. D-8

Comment: The preamble to the proposed method states that it has few interferences. We have found that calcium and sulfate particulate from

some lime kilns and recovery furnaces are severe interferences. These compounds should be noted in the applicability section. Provisions should be made to place a filter in the sample train to remove particulate matter.

Response: The sampling train has been modified to include a filter. Proper use of the filter to eliminate particulate interferences is now mentioned in the applicability section.

16. D-8

Comment: The sample analysis procedure should be changed to follow Method 6 exactly. The proposed procedure generates a large titration volume with only enough sample for one analysis.

Response: The sample analysis procedure has been changed to reduce the large titration volume and allow for duplicate analysis. The small sample aliquot specified by Method 6 would create a dilute sample wherein analytical accuracy would be lowered due to the decreased amount of titrant required.

17. D-8

Comment: The preamble to the method states several advantages of Method 16A over Method 16. The following comments are made.

a. It is stated that no gas dilution system is needed. A gas dilution system is required for the system performance check.

b. We disagree that samples need not be analyzed in the field. Due to the need to check system performance prior to, during, and after testing, all samples must be analyzed on site, and all results must be calculated at that time.

c. The proposed method will not necessarily reduce the cost of emission testing to demonstrate compliance with the standards. Our experience with Method 16 and 16A indicates that Method 16A requires 80- to 100-labor hours to test a source whereas Method 16 would require 40 labor hours to test the same source.

Response: The dilution system mentioned in the preamble refers to the collection of the sample gas. A gas dilution system is used in the system performance check but is not needed while collecting samples. The method makes no requirement to analyze any samples in the field. It is wise to analyze the system performance samples in the field to determine the validity of the samples, but this is not mandatory. We agree that the amount of time required to use a test method depends on the proficiency of the tester. If it is determined by individuals that Method 16A is more costly and time consuming than Method 16, then the individual has the option of not using the alternative method.

18. D-1

Comment: The new method is a welcome change. We agree with the five advantages noted in the preamble and as an additional advantage, the availability of this technique in lieu of such traditional methods as the continuous titrimetric techique which has been plagued with frequent equipment malfunctions in field applications.

Response: No response needed.

19. D-8

Comment: We calculate the minimum detectable limit for the method to be 1 ppm instead of 0.04 ppm.

Response: Minimum detectable limits of 0.3 ppm for 1-hour samples and 0.1 ppm for 3-hour samples based on the blank volume plus two standard deviations have been calculated and will be listed.

20. D-8

Comment: The ±2 percent flowmeters specified in Section 2.1.4 are excessive. A flow rate of 2 liters ±10 percent is sufficient.

Response: The 2 percent specification refers to flowmeter accuracy, not flow rate precision. This has been clarified by rephrasing the sentence.

21. D-8

Comment: The combustion gas in Section 3.1.5 should be air only since dry gas meters are not calibrated for oxygen.

Response: Calibration of the dry gas meter is independent of gas type. One liter of oxygen would occupy the same volume as 1 liter of air. The dry gas meters are no longer used in the system performance check.

22. D-8

Comment: The system performance check should be performed before any cleaning of the system is done.

Response: We agree, and this has been stated in Section 4.1.4.

23. D-8, D-9

Comment: Based on past studies with Method 16A, the 5 percent precision for the system performance check is too stringent. This is also unnecessarily restrictive for those sources which generally operate well below the applicable standard. Precision within 10 percent and the option to run the system performance check at the level of the applicable standard ±20 percent is more reasonable.

Response: The precision requirement for the system performance check has been dropped. An allowance to run this check at the level of the applicable standard $\pm$ 20 percent has been made.

24. D-8

Comment: The audit samples in Section 5.2 should be used to validate the SO_2 titration but should not be needed as a substitute for a recovery check.

Response: The original intent of this audit requirement was to substitute an unknown H_2S gas audit for one of the recovery checks during a test. This requirement has been dropped in favor of an SO_2 audit of the analysis procedure.

25. D-9

Comment: Method 16 measures TRS concentration on a dry basis. If oxygen correction is needed (as required for most kraft sources), Method 3 should be specified to determine the oxygen content of the sample on a dry basis.

Response: Use of Method 3 is already specified in paragraph 60.285 of the regulations.

26. D-9

Comment: Since the present TRS standards require O_2 correction of the measured TRS concentration for most sources, the calculation procedure for O_2 correction should be added to the method.

Response: The equation for O_2 correction is listed in paragraph 60.284 of the regulations.

27. D-10

Comment: The proposed method should be revised to allow the use of 6 percent hydrogen peroxide and large impingers containing 200 ml of absorbing solution.

Response: The use of large impingers in this method would be impractical. A large titration volume would result form taking an aliquot of sufficient size to analyze accurately. A 200-ml sample aliquot, plus 800 ml of isopropanol, means titrating a 1-liter sample.

28. D-10

Comment: Section 4.2 should be revised as follows: "Pour contents of the impingers of the Method 6 part of the train into separate leak-free polyethylene bottles."

Response: The impinger contents of the Method 6 part of the train should be poured into a container separate from the contents of the spent scrubber impingers. The individual Method 6 impinger contents need not be placed in separate bottles since the combined contents are used in the analysis.

29. D-8

Comment: In Section 6.2, 12.020 µ/meq should be 12.020 µl/meq.

Response: This correction has been made. This factor has been converted to 12025 µl/meq to allow $V_{m(std)}$ to be expressed in dry standard liters instead of dry standard cubic meters.

30. D-8

Comment: The preamble to the method states that Method 16A reduces the chances of measurement error because it involves fewer and less complicated components. We think the chance of measurement error using

Method 16A is greatly increased due to potential interferences (calcium particulate) from the source, the components required for checking system performance, and the method specified for calibration of the calibration gas cylinder. The method should be modified and further field evaluations should be performed to demonstrate that the method gives comparable results to Method 16.

Response: The potential interferences from the source have been eliminated by incorporating a filter into the sampling train. The components required to check the system performance have been simplified by allowing the use of permeation devices and rotameters to determine dilution ratios. The permeation devices offer an alternative to calibration gas dilution and verification of concentration by Method 11. In a recent evaluation of Method 11 by the Agency, the accuracy of Method 11 was verified down to a concentration of 2 ppm. Method 16A has been shown by the EPA and other companies to give results comparable to Method 16.

31. D-1, D-3, D-4, D-7

Comment: We approve of and support the proposed method for the following reasons:

a. Method 16A is superior to Method 16 and provides more accurate data at a lesser expense.

b. The unnecessary complexity of emission testing is reduced.

c. Plants will have the option of using their own staff and equipment at a considerable savings over using expensive outside consultants having the specialized equipment and instrumentation required by existing Method 16.

Response: No response needed.

Table 1. LIST OF COMMENTERS

Docket Number A-80-38

Document number	Commenter/affiliation
IV-D-1	Peter E. DeRossi, Corporate Environmental Engineer Green Bay Packaging, Inc. Post Office Box 1107 Green Bay, Wisconsin 54305
IV-D-2	Michael E. Fogle, Unit Coordinator Georgia Department of Natural Resources 270 Washington Street, S.W. Atlanta, Georgia 30334
IV-D-3	Jay Lipscomb Mostardi-Platt Associates, Inc. 1077 Entry Drive Bensenville, Illinois 60106
IV-D-4	T.C. Owen, Corporate Director Union Camp Corporation Post Office Box 1391 Savannah, Georgia 31402
IV-D-5	C.D. Malloch, Regulatory Management Director Monsanto Company 800 N. Lindberg Blvd. St. Louis, Missouri 63166
IV-D-6	Alan S. Rosenfeld, Sr. Research Engineer Crown Zellerbach Environmental Services 904 N.W. Drake Street Camas, Washington 98607
IV-D-7	Karl C. Ayers, Energy and Environmental Manager Mead Eighth and Hickory Streets Chillicothe, Ohio 45601
IV-D-8	Bruce B. Ferguson, Vice President, Analytical Services Harmon Engineering and Testing Auburn Industrial Park Auburn, Alabama 36830

Table 1. LIST OF COMMENTERS

(Continued)

Docket Number A-80-38

Document number	Commenter/affiliation
IV-D-9	Russell O. Blosser, Technical Director National Council of the Paper Industry for Air and Stream Improvement, Inc. 260 Madison Avenue New York, New York 10016
IV-D-10	Bill Stewart, Executive Director Texas Air Control Board 6330 Hwy. 290 East Austin, Texas 78723